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54 Cycloalkyl-type isotropic dyes for liquid crystal display devices.

57 Certain cycloalkyl-type compounds have been found to be useful as isotropic dyestuffs in guest-host combinations with nematic, cholesteric and smectic liquid crystals and other well-known dichroic dyestuffs. By "isotropic" it is meant that the disclosed dyestuffs have optical order parameters (S) very close to zero. Use of the disclosed isotropic dyestuffs with additional well-known dichroic dyes in liquid crystal display devices, provides displays which alter between one colored state and another, depending upon the presence or absence of an electric field across the display.

CYCLOALKYL-TYPE ISOTROPIC DYES  
FOR LIQUID CRYSTAL DISPLAY DEVICES

Technical Field

This invention relates to guest-host combinations of isotropic cycloalkyl dyestuffs and well-known dichroic dyestuffs, with nematic, smectic and cholesteric liquid crystals. This invention further relates to electro-optical devices employing such guest-host combinations. Use of the isotropic dyes disclosed with additional well-known dichroic dyes provides electro-optical devices which are capable of alternating between one colored state and another depending upon the presence or absence of an electric field.

Background Art

The use of dichroic dyes in solution with various liquid crystal materials, and liquid crystal display devices incorporating such mixtures are well-known in the art. These dichroic dye-liquid crystal mixtures may be used in "guest-host" type liquid crystal displays or, when an optically-active additive is employed, in "phase-change" type liquid crystal displays. Additionally, dichroic dyes may be utilized in smectic liquid crystal display devices as disclosed in U.S. Patent No. 4,196,974, and commonly assigned U.S.S.N. 251,247, filed April 6, 1981 and U.S.S.N. 436,020 filed October 22, 1982, (Attorney's Docket File No. 32,942).

Many of these dichroic dyes are elongated molecules which exhibit little or no absorption of light vibrating parallel to the long axis, while absorbing that light in various portions of the visible spectrum which vibrates perpendicular to the long axis. Other dichroic dyes may align oppositely, being colorless (non-absorbing)

with respect to light vibrating parallel to the short axis of the molecule and colored (absorbing) with respect to light vibrating perpendicular to the short axis.

In the above-mentioned types of displays the host liquid crystal material has its orientation controlled by the application of electric fields and in turn interacts with the guest dichroic dye to induce a cooperative conforming alignment. The dichroic dye manifests low or high absorbance of incident light depending upon its molecular orientation with respect to the light wave vector. Thus, generally when an electric field is applied to the display, the area between the electrodes appears clear, i.e., all the dyes exhibit minimum absorption, and in the absence of an electric field, the display appears characteristically dye colored, i.e., the dyes are in a high absorbing state.

It is known that by combining two different dichroic dyes, one which absorbs light parallel to the short axis of the molecule, and one which absorbs light parallel to the long axis of the molecule, devices which change from one color to another are possible. It has also been disclosed in U.S. Patents 4,105,299 and 4,154,746 that an isotropic, i.e., nondichroic dyestuff, could be combined with a dichroic dyestuff so that the colors of the two would be additive at one stage, and the color of the isotropic dyestuff would appear at the other stage of the electric field cycle, so that a device which changes from one color to another would be possible. One difficulty in providing two-color displays by utilizing isotropic dyes has been to find dyes which are not only isotropic, but which are non-ionic, have acceptable extinction coefficients, sufficient solubility in liquid crystal materials, and good photostability.

Disclosure of Invention

The isotropic dyes of this invention are particular types of substituted cycloalkyl compounds. These isotropic dyes have measured optical order parameters, S, of about  $0 \pm 0.1$ . Additionally, the isotropic dyes of this invention have extinction coefficients greater than about  $1 \times 10^4$ , solubilities in nematic, cholesteric and smectic liquid crystal materials in excess of about 0.1 percent by weight, and good chemical, photochemical and electrochemical stability.

The isotropic dyes disclosed are molecules which do not exhibit a preference for aligning in liquid crystal material along any particular axis. This is due to the fact that the molecules do not have a long and short axis, but have axes which are of near equal length. Thus, the isotropic dyes of this invention are capable of absorbing substantially the same amount of substantially the same wavelengths of incident light regardless of the molecular orientation of the dye molecules with respect to the light wave vector.

Detailed Description

The isotropic dyes of this invention have the general formula:



wherein:

Y is independently an anthracene-one group, a phthalate group, or a quinonoid benzene ring having one or two alkyl substituents of about 1 to 20 carbon atoms in the ortho position (s) relative to the oxygen of the quinonoid benzene ring;

C is a cyclopropyl or cyclobutyl ring;

X is independently Y or an oxygen atom;

n is 1 to 3 when C is a cyclopropyl group, and 1 to 4 when C is a cyclobutyl group; and

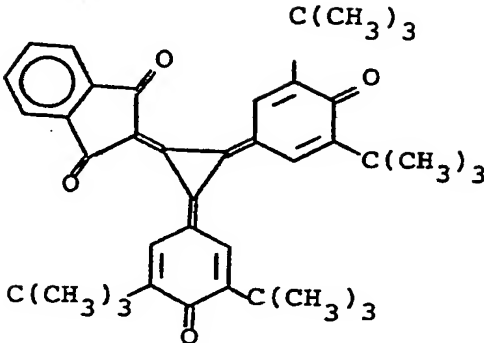
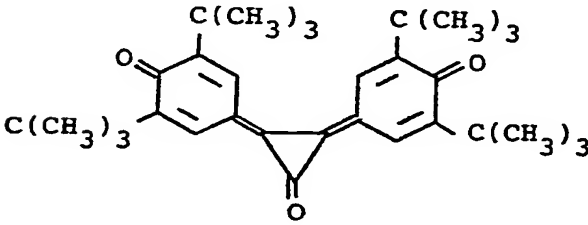
m is 3-n when C is a cyclopropyl group, and 4-n when C is a cyclobutyl group.

Exemplary of the preferred cycloalkyl-type isotropic dyestuffs are those compounds listed in Table I,  
5 hereinbelow:

TABLE I

Dye Structure	S in ROTN 404'	$\lambda_{\max}$ in ROTN 404' (nm)
	$0 \pm 0.1$	640
<p>5 (a cyclopropyl isotropic dyestuff with quinonoid benzene ring substituents)</p>	$0 \pm 0.1$	560
<p>(a cyclobutyl isotropic dyestuff with quinonoid benzene ring substituents)</p>	$0 \pm 0.1$	670
<p>(a cyclopropyl isotropic dyestuff with anthracene-one substituents)</p>		
<p>"ROTN 404" is a eutectic mixture of biphenylpyrimidine liquid crystals commercially available from Hoffman LaRoche Co.</p>		

TABLE I Continued

<u>Dye Structure</u>	<u>S in ROTN</u> <u>404</u>	<u><math>\lambda_{\text{max}}</math> in ROTN</u> <u>404 (nm)</u>
	$0 \pm 0.1$	450 and 650
<p>5 (a cyclopropyl isotropic dyestuff with quinonoid benzene ring and phthalate ring substituents)</p>		
	$0 \pm 0.1$	560
<p>10 (a cyclopropyl isotropic dyestuff with quinonoid benzene ring and oxygen substituents)</p>		

The isotropic dyes of this invention may be synthesized by the Friedel-Krafts condensation using aryl alcohols and aluminum chloride complexed cyclopropenium moieties in inert solvents, followed by oxidation of the resultant compound to the appropriate cycloalkyl isotropic dye. Preferably, the cyclobutyl dyes of the present invention are prepared by the dimerization of the appropriate bis-aryl acetylene, followed by oxidation to the cycloalkyl isotropic dye.

The preparation of these cycloalkyl compounds is found, for example, in numerous articles published by Dr. Robert West and his associates at the University of Wisconsin. These articles include "Triarylcyclopropenium Ions and Diarylcyclopropenones from Trichlorocyclopropenium Ion," Robert West et al., J.A.C.S., Vol. 92, No. 1, Jan. 14, 1970, pp. 149-154; "Diquinocyclopropenes and Triquinocyclopropanes," Robert West et al. J.A.C.S., Vol. 92, No. 1, Jan. 14, 1970, pp. 155-161; "Synthesis of a Diquinocyclopropanone and a Diquinoethylene," Robert West et al., J.A.C.S. 89:1, January, 1967, p. 153, and "Triquinocyclopropanes," Robert West et al., J.A.C.S. 88:6, p. 11. All of these articles are incorporated herein by



reference.

The isotropic dyes of the present invention have absorption maxima at wavelengths between about 400 and 700 nanometers. The absorption maxima for several of the preferred isotropic dyes have been shown in Table I, hereinabove.

The isotropic dyes of the invention have optical order parameters  $S$  which are very close to zero. The optical order parameter is a measure of the efficiency with which the dye is oriented by the liquid crystal material. The determination of the optical order parameter,  $S$ , is discussed in Journal of Applied Physics, Vol. 45, No. 11, 4718-23 (1974).

$$S = \frac{A_0 - A_1}{A_0 + 2A_1}$$

wherein:

$A_0$  is the absorbance in the absence of an electric field; and

$A_1$  is the absorbance in the presence of an electric field.

Since the isotropic dyes of this invention are not aligned along any particular axis by the liquid crystal materials, their absorptivity is not dependent upon the presence or absence of an electric field and their optical order parameters are very close to zero, i.e., about  $0 \pm 0.1$ .

The dyes of the invention have relatively high molar extinction coefficients. The molar extinction coefficient is a measurement of the extent to which the dye absorbs light at any particular molar concentration. A dye with a relatively higher molar extinction coefficient provides a display with better brightness characteristics, at any particular molar concentration of dye, than does a dye which has a relatively lower molar extinction coefficient. The extinction coefficients of the isotropic dyes of the invention are generally greater than about  $1 \times 10^4$ .

The isotropic dyes of the invention are chemically, photochemically and electrochemically stable. For example, the isotropic dyes of the invention remain stable even after greater than about  $3 \times 10^5$  hours of exposure to ultraviolet radiation.

In order for isotropic dyes to be useful in liquid crystal display devices, the dye molecule must have suitable solubility in the host liquid crystal material. Solubilities of greater than about 0.1 percent by weight insure that the dye will have sufficient absorptivity to be useful in displaying its characteristic color. The dyes of the present invention have solubilities in most well-known nematic, smectic and cholesteric liquid crystals of greater than about 0.1 percent by weight.

The host liquid crystal material may be any nematic, smectic or cholesteric liquid crystal compound which is per se known in the art. The nematic liquid crystals can have either a positive or negative dielectric anisotropy. As used herein the term "positive" or "negative" refers to the net dielectric anisotropy where mixtures are used. Generally liquid crystals having higher absolute values of dielectric anisotropy are preferred. At this time the positive nematic materials having high dielectric anisotropy are more readily available. Mixtures of positive and negative materials are also useful, particularly those mixtures having a net positive dielectric anisotropy.

Readily available positive nematic liquid crystal materials which have been found suitable include trans-4-n-pentyl-(4'-cyano-phenyl)-cyclohexane, trans-4-n-pentyl-(4'-cyano-biphenyl)-4-cyclohexane, p-n-hexylbenzylidene-p'-amino-benzonitrile, p-methoxybenzylidene-p'-amino-benzonitrile, p-ethoxybenzylidene-p'-amino-benzonitrile, p-cyano-benzylidene-p'-n-butyoxylaniline, p-cyanobenzylidene-p'-octyloxylaniline, 4-cyano-4'-alkyl(or alkoxy)biphenyl, 4-cyanophenyl-4'-alkyl(or alkoxy)benzoate, 4-alkyl(or alkoxy)phenyl-4'-cyanobenzoate, and the family

of alkyl phenyl pyrimidines.

Eutectic mixtures and combinations are also useful. Illustrative are eutectic mixtures of 4'-substituted-4-cyanobiphenyl wherein the 4' substituents are alkyl or alkoxy of 3 to 12 carbon atoms, and terphenyl liquid crystals. Representative is the commercially available "E7" mixture from B.D.H. Ltd. Another useful mixture is commercially available from Hoffman LaRoche under the trade name "ROTN 404." "ROTN 404" is a eutectic mixture of biphenyl pyrimidine liquid crystals. Yet another useful mixture of compounds comprises mixtures of the phenylcyclohexanes referred to above such as mixtures comprising the 4-alkyl-(4'-cyanophenyl)cyclohexanes, mixtures comprising 4-alkyl-(4'-cyanobiphenyl)cyclohexanes, and mixtures comprising both types of compounds. One useful commercial mixture is identified as Nematic Phase 1132 TNC "Licristal" or "PCH 1132" from Hoffman LaRoche, Inc.

Representative of nematic liquid crystals having negative dielectric anisotropy which would be useful in the present invention is the liquid crystal "EN-18" available from Chisso Corporation.

Representative cholesteric liquid crystals which are useful in the practice of the present invention include cholesterol benzoate, cholesterol nonanoate, cholesterol chloride, cholesterol hexanonanoate, and 4-(+)(2-methylbutyl)-4'-cyanobiphenyl.

Representative smectic liquid crystals which are useful in the practice of the present invention include the well-known cyano biphenyls or esters of substituted cyano biphenyls, for example, p-(N)octyloxy-p'-cyano biphenyl and bis(p,p')(N)-pentyloxy-phenyl benzoate.

The isotropic dyes of the invention may be utilized along with other well-known dichroic dyes in numerous types of liquid crystal displays. The construction of "guest-host" type liquid crystal displays is described in Applied Physics Letters, Vol. 13, pages 91-92 (1968), incorporated herein by reference.

"Phase-change" type displays are described by D. L. White and G. N. Taylor in "New Absorptive Mode Reflective Liquid Crystal Display Device," Journal of Applied Physics, Vol. 45, pp. 4718-4723, (1974), also incorporated herein by reference. Briefly both types of devices comprise a typical transmissive or reflective liquid crystal display cell having appropriate front and back electrode patterns and featuring a homogeneously or homeotropically oriented liquid crystal layer comprising host positive nematic liquid crystal, and a guest dichroic dye. In "phase-change" type displays an optically-active dopant is present in amounts sufficient to provide a cholesteric or helically ordered liquid crystal phase. The "host" liquid crystal material has its orientation controlled by the application of electrical fields and in turn interacts with "guest" dichroic dye molecules to induce a cooperative conforming alignment.

Normally, "guest-host" type displays in the "off" state (no electric field present) require one polarizer to absorb one polarization of incident light while the guest dichroic dye material in the display absorbs the other polarization. In the presence of an electric field, the host liquid crystal material, and thus the guest dichroic dye, are generally oriented by the electric field so that the dichroic dye molecules assume their essentially nonabsorbing state. In this state, the dichroic dye is oriented to absorb relatively little incident light, and a "clear" area, corresponding to the electrode area, on a background, corresponding to the characteristic color of the dichroic dye, is observed. By selective activation of the electrodes, information can be readily displayed.

In "phase-change" type displays the helical ordering of the host liquid crystal material is superimposed upon the dichroic dye. The helically ordered dichroic dye is thus able to absorb both polarizations of incident light thereby producing a brighter display since no auxiliary polarizers are required, as they are in the "guest-host" type displays. In the absence of an electric

field across the display electrodes, the dichroic dye is oriented to absorb a substantial amount of the unpolarized incident light and the display area exhibits a color characteristic of the dichroic dye. When an electric field is applied to the desired electrode, the liquid crystal layer in register with the electrode is caused to change from a cholesteric phase to a nematic phase, generally in homeotropic alignment due to the positive dielectric anisotropy of the liquid crystal host material. In this state, the dichroic dye in the liquid crystal layer is oriented to absorb relatively little incident light, and a "clear" area, corresponding to the electrode area on a colored background, is observed.

When an isotropic dye of the present invention is included in a "guest-host" or "phase-change" type display a two-color display is produced. When the electric field is off both the isotropic and the dichroic dyes absorb incident light, and an additive color due to both dyes is observed. When an electric field (at or above the threshold level) is applied ("on" state), the dichroic dye assumes its essentially nonabsorbing state while the isotropic dye absorption is almost unchanged and a color which is characteristic of the isotropic dye alone appears. As a result, different colored states can be achieved.

Additionally, the isotropic dyes of the invention have proven to be particularly useful in combination with helichromic compounds in helichromic-type liquid crystal displays. Helichromic compounds and displays are disclosed in copending U.S. Patent Application Serial No. 274,184, filed June 22, 1981, incorporated herein by reference. These displays are constructed in the same manner as the "phase-change" type displays, except that a helichromic compound, having both a chromophoric moiety and an optically-active moiety is used to replace both the dichroic dye and the optically-active dopant. Helichromic compounds are organic, nonionic, nonliquid-crystalline compounds which are soluble in nematic, cholesteric and smectic liquid crystal materials. Helichromic compounds

are capable of being aligned by liquid crystal materials, and are capable of performing as circularly dichroic dyes when used in liquid crystal display devices. In helichromic-type displays the helichromic compound is used  
5 in amounts sufficient to insure that incident light is propagated in a circularly polarized manner, so that all polarizations of the incident light are absorbed.

In the helichromic displays, in the absence of an electric field across the display electrodes, the  
10 helichromic compound is oriented to absorb a substantial amount of the unpolarized incident light and the display exhibits a color which is characteristic of the helichromic compound. When an electric field is applied to the desired electrodes, the liquid crystal layer in register with the  
15 electrodes is caused to change to a nematic phase, generally in homeotropic alignment. In this state the helichromic compound in the liquid crystal layer is oriented to absorb relatively little incident light, and a "clear" color is observed in the area corresponding to the  
20 electrode area.

When an isotropic dye of the invention is included in a helichromic display a two-color display is produced. When the electric field is off both the isotropic dye and the helichromic compound (which is itself  
25 a circularly dichroic dye) absorb incident light, and an additive color due to both dyes is observed. When an electric field is applied at or above the threshold level, the helichromic compound assumes its non-absorbing state, and a color characteristic of the isotropic dye alone is  
30 observed.

Yet another use for the isotropic dyes of the invention is in thermally-addressed smectic liquid crystal display devices, as described in U.S. Patent No. 4,196,974 and U.S.S.N. 251,247, filed April 6, 1981, both of which  
35 are incorporated herein by reference. Generally, a thermally-addressed smectic liquid crystal display device comprises a typical transmissive or reflective liquid crystal display having appropriate front and back electrode patterns and featuring a smectic liquid crystal medium

including at least one dichroic dye of high order parameter. The liquid crystal medium is thermally sensitive and has a transition between an upper thermal state and a lower smectic phase. The upper thermal state  
5 is either a nematic or isotropic state, or, where the liquid crystal medium includes at least one cholesteric liquid crystal compound, a cholesteric state. The device is operated by heating the medium to its upper thermal state. The medium is then rapidly cooled while a portion of the  
10 mixture is addressed by the application of an electric field. A homeotropic light transmissive state is normally developed in the portions of the mixture which are addressed by the electric field, while a light absorbing state develops in the unaddressed portions of the mixture.  
15 The dichroic dye in the portion of the mixture which is unaddressed, absorbs incident light passing through the medium; the liquid crystal medium acting as a vehicle to orient the dichroic dye molecules into a light absorbing position. Electrodes are provided adjacent the liquid  
20 crystal medium, and heating electrodes are also provided to heat the medium to the upper thermal phase. By selective activation of the electrodes, information can be readily displayed.

When an isotropic dye of the present invention is  
25 included in the smectic liquid crystal medium, along with the dichroic dye, a two-color display can be produced. After heating the medium to its upper thermal state, in those portions of the medium which are allowed to cool in the absence of an electric field, both the isotropic and  
30 dichroic dyes will absorb incident light, and an additive color due to both dyes appears. In those portions of the medium which are allowed to cool in the presence of an electric field, the dichroic dye absorption is minimal, while the isotropic dye absorption is almost unchanged, so  
35 that a color due to the isotropic dye alone appears.

Furthermore, the isotropic dyes of the invention can be utilized in the more recently discovered helichromic-smectic liquid crystal displays which are described in commonly assigned co-pending U.S.S.N.

436,020, filed October 22, 1982 (Attorney's Docket File No. 32,942), incorporated herein by reference. The helichromic-smectic liquid crystal display is constructed and operated in the same manner as the smectic liquid  
5 crystal displays described hereinabove, except that a helichromic compound, having a chromophoric moiety and an optically-active moiety is used to replace both the dichroic dye and any cholesteric material.

When an isotropic dye of the present invention is  
10 included in a helichromic-smectic liquid crystal display device, and the medium is heated to its upper thermal state (called a helichromic state), those portions of the medium which are allowed to cool in the absence of an electric field appear as an additive color, due to the absorbance of  
15 both the helichromic compound and the isotropic dye. Those portions of the medium which are allowed to cool in the presence of an electric field appear a color which is characteristic of the isotropic dye alone.

The concentration of isotropic dye which is  
20 useful in all of the above-described types of liquid crystal displays is between about 0.1 and 5 percent by weight of the liquid crystal materials. Preferably the concentration of isotropic dye is between about 1.0 and 3.0 percent by weight, for optimal color characteristics.

25 The various dichroic dyes or helichromic compounds of the prior art, which are advantageously used to provide two-color liquid crystal displays, have absorption maxima between about 400 and 750 nm. Preferably also, the dichroic dyes or helichromic compounds have  
30 optical order parameters (S) of greater than about 0.5, in order to insure displays having high contrasts and brightness.

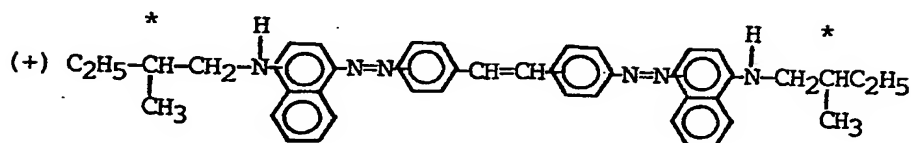
Suitable dichroic dyes of the prior art are well-known azo, azo-stilbene, benzothiazolylpolyazo  
35 methine, azomethine, merocyanine, methine-arylidene, tetrazine, oxadiazine, carbazole-azo or anthraquinone type dichroic dyes, such as those disclosed in U.S. Patent Nos. 4,145,114; 4,128,497; 4,179,395; and in Applicants' copending U.S. Serial No. 70,421 filed August 28, 1979.



Exemplary well-known dichroic dyes which are useful when combined with the isotropic dyes of the present invention are shown in Table II, hereinbelow.

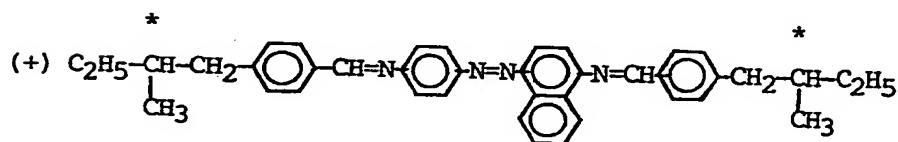


Exemplary helichromic compounds which are useful when combined with the isotropic dyes of the present invention are shown hereinbelow.



5

$\lambda_{\text{max}}$  in ROTN 404 = 550 nm



$\lambda_{\text{max}}$  in ROTN 404 = 440 nm

The concentration of the dichroic dye (or helichromic compound) which is useful in the "guest-host", "phase-change" "helichromic" and "smectic" type liquid crystal displays is between about 0.1 and 5 percent by weight of the liquid crystal material. A preferred concentration is between 1 and 2 percent by weight in order to achieve optimal contrast and brightness. Of course, the maximum amount of dichroic dye which can be present is dependent upon the solubility of the dye in the liquid crystal materials.

The ratio of the dichroic dye to the isotropic dye present in the display is preferably that which will cause the absorption of light by the dichroic dye to be at least equivalent to the absorption of light by the isotropic dye. This is accomplished by adjusting the concentration of each individual dye so that the absorbance at the wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) for each dye is approximately equal.

Generally, the ratio of dichroic dye concentration to isotropic dye concentration is between about 1:5 to 5:1, depending upon the molar extinction coefficient of each dye and the desired optical contrast.

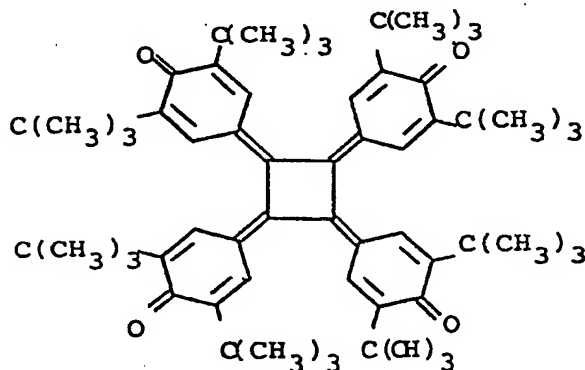
The following examples illustrate compositions and devices in accordance with the invention. The optical order parameters (S), and max were measured in ROTN 404.

Example 1

5 A helichromic type liquid crystal display which is bright orange in the absence of an electric field and is magenta in the presence of an electric field was constructed as follows:

10 A display cell was assembled comprising two opposing glass plates coated on their interior surfaces with tin/indium oxides to form a conductive electrode pattern. Overlaying the electrode pattern, a homeotropic orientation layer was created by the vapor deposition of a dielectric silicon monoxide layer about 100 Å thick, at an  
15 angle greater than 30°. The cell was provided with a reflectorized backing, and had a 12 μm cell spacing.

The cell was filled with a mixture of 0.98 grams of a eutectic mixture of biphenylpyrimidine liquid crystals (commercially available as "ROTN 404" from Hoffman LaRoche  
20 Co.), 0.01 grams of the isotropic dye.

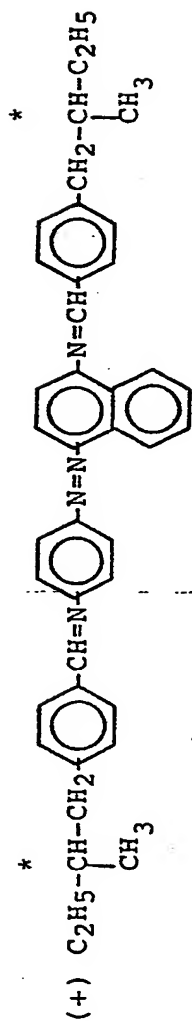


(octa-t-butyl tetraquino cyclobutane)

and 0.01 grams of the helichromic compound

$$\frac{\lambda_{\max}(\text{nm})}{\text{nm}}$$

440



The isotropic dye was prepared by dissolving 0.1 mole of bis(2,6-ditertiary butyl)-4,4'-dihydroxy acetylene in one liter diglyme and heating this solution to 180°C in the presence of a lead tetra-acetate catalyst. Dimerization  
5 of the acetylene occurred and the crude product was separated, oxidized in an alkaline potassium ferricyanide solution and recovered by the addition of triphenylamine. The product was purified by crystallization from benzene.

The helichromic compound was prepared according  
10 to the procedure described in commonly assigned copending U.S.S.N. 251,247, filed April 6, 1981, incorporated herein by reference.

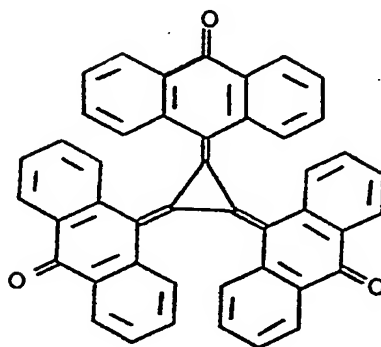
Electrical contacts were made to the indium/tin oxide coating and these were connected to a switching  
15 circuit including a source of low voltage alternating current capable of providing an RMS voltage of 20 volts, 1 kHz. In the absence of a voltage the cell exhibited absorbance maxima at 440 and 560 nm and appeared bright orange in color. In the presence of a voltage the  
20 helichromic compound assumed a low absorbance orientation in the cell and the cell exhibited maximum absorbance only at about 560 nm. The cell in the voltage "on" state appeared magenta in color. Thus, a satisfactory two-color helichromic type liquid crystal display was produced.

25

#### Example 2

A helichromic type liquid crystal display which was green in the absence of an electric field and blue in the presence of on electric field (greater than the threshold voltage) was constructed as in Example 1.

The fill mixture used was that of Example 1, except that the isotropic dyestuff.



<u>S</u>	<u><math>\lambda_{\max}</math> (nm)</u>
$0 \pm 0.1$	670

5 was substituted for the the isotropic dyestuff of Example 1.

This isotropic dye was prepared by mixing one equivalent of tetrachlorocyclopropane with one equivalent of  $\text{AlCl}_3$  and warming this mixture momentarily at  $80^\circ\text{C}$  to form tetra-chlorocyclopropenium-tetra-chloroaluminate. Two  
 10 equivalents of 9-anthrone was then added and the reaction mixture was stirred for about 30 minutes. The resulting deep violet reaction mixture was poured into water and stirred until the color was discharged. The solution was filtered and recrystallized from ethanol-ether. The  
 15 product was extracted with chloroform and dried over  $\text{MgO}_2$ .

One equivalent of 9 anthrone was added to the filtered chloroform solution and the mixture was heated to  $50^\circ\text{C}$ . The reaction product was extracted with several portions of chloroform, dried, filtered and stripped of  
 20 solvent. The product was dissolved in acetonitrile and triethylamine was added to convert the crude material to the triquinocyclopropane product. The product was recovered by precipitation with ethanol, filtered, washed and dried.

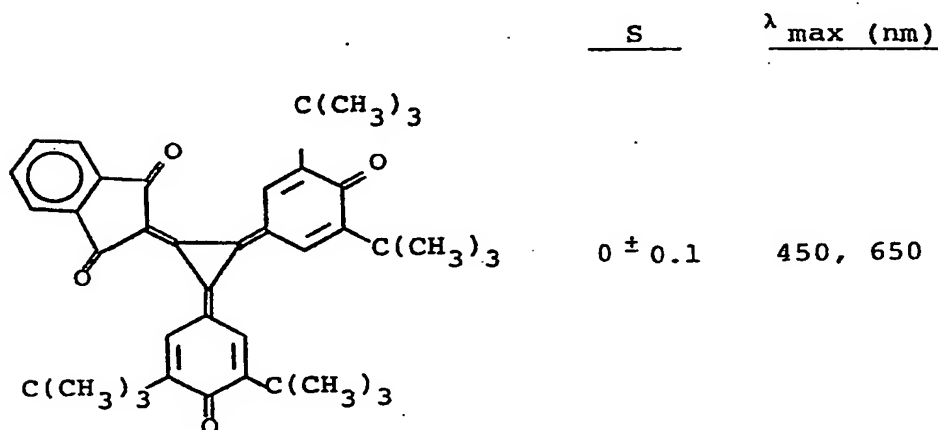
25 In the absence of a voltage across the cell, it exhibited absorbance maxima at 440 and 670 nm, and appeared green in color. In the presence of a voltage, the cell had

an absorption maximum at about 670 nm, and appeared blue. This blue color was due solely to the isotropic dye, since the helichromic compound was in its low absorbance orientation. Thus, a satisfactory two-color helichromic type liquid crystal display was produced.

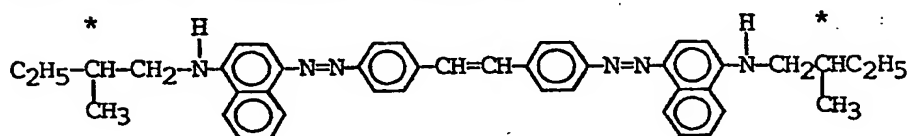
### Example 3

A helichromic type liquid crystal display which was black in the absence of an electric field and maroon in the presence of an electric field (greater than the threshold voltage) was constructed as in Example 1.

The fill mixture used was that of Example 1, except that the isotropic dyestuff.



was substituted for the isotropic dyestuff of Example 1. And, the helichromic compound



$\lambda_{\max}$  in ROTN 404 = 550 nm

was substituted for the helichromic compound of Example 1.

This isotropic dye was prepared by mixing one equivalent of tetrachloro-cyclopropane with one equivalent of  $\text{AlCl}_3$  and warming this mixture momentarily at  $80^\circ\text{C}$  to form tetrachlorocyclopropenium tetrachloroaluminate. Two equivalents of 2,6-bis-tertiary butylphenol was then added and the reaction mixture was stirred for about 30 minutes.



The resulting deep violet reaction mixture was poured into water and stirred until the color was discharged. The solution was filtered and recrystallized from ethanol-ether. The product was extracted with chloroform and dried over  $MgO_2$ .

One equivalent of benzene carboxylic anhydride was added to the filtered chloroform solution and the mixture was heated to  $50^{\circ}C$ . The reaction product was extracted with several portions of chloroform, dried, filtered and stripped of solvent. The product was dissolved in acetonitrile and triethylamine was added to convert the crude material to the triquinocyclopropane product. The product was recovered by precipitation with ethanol, filtered, washed and dried.

The helichromic compound was prepared according to the procedure described in copending U.S.S.N. 251,247.

In the absence of a voltage across the cell, it exhibited absorbance maxima at 450, 550 and 650 nm, and appeared black in color. In the presence of a voltage, the cell had an absorption maximum at about 440 and 650 nm, and appeared maroon. This maroon color was due solely to the isotropic dye, since the helichromic compound was in its low absorbance orientation. Thus, a satisfactory two-color helichromic type liquid crystal display was produced.

25

#### Example 4

A thermally addressed smectic/cholesteric liquid crystal display, which appears bright blue when in the "off" state, and bright green when a heating pulse is applied, was constructed as follows:

30

A display cell was assembled comprising two opposing glass plates. The bottom substrate was coated on its interior surface with an aluminum coating having 0.1 ohms per square resistance. This aluminum coating forms the row heating electrode and the bottom addressing electrode. The top substrate was coated with an 0.1 micrometer thick coating of indium/tin oxide, to form a thin conductive transparent column addressing electrode.

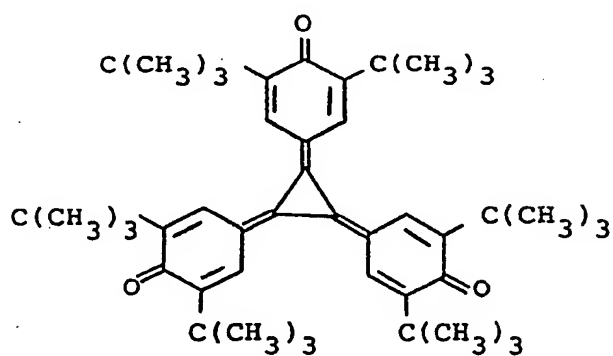
35

Overlaying the electrodes, a homeotropic orientation layer was created by the vapor deposition of a dielectric silicon monoxide layer about 100 Å thick, perpendicular to the glass plates. The cell had a spacing of 15 μm.

- 5 The cell was filled with a mixture comprising 0.93 g of the nematic liquid materials of Example 1, 0.7 g of the cholesteric additive (+)4-(2-methylbutyl)-4'-cyano biphenyl, and the indicated amounts of the following smectic liquid crystal materials:

10	$\text{H}_{21}\text{C}_{10}-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	1.48 g
	$\text{H}_{25}\text{C}_{12}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	3.06 g
	$\text{H}_{21}\text{C}_{10}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	1.32 g
	$\text{H}_{17}\text{C}_8-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	2.51

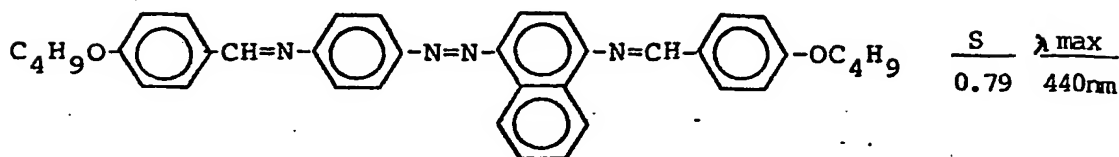
- 15 to which was added 0.5 percent by weight of the isotropic dye,



S    λ<sub>max</sub>

0    0.1    620

and 1.0 percent by weight of the dichroic dye



This dichroic dye is commercially available from Nippon Kankoh-Shikiso Kenkyusho, Okayama, Japan.

5           The isotropic dye was synthesized by  
Friedel-Krafts condensation of the complex formed by the  
introduction of 1 mole equivalent of anhydrous aluminum  
chloride and 1 mole equivalent of tetrachlorocyclopropane  
in nitrobenzene to 3 mole equivalents of 2,5-bis-t-butyl  
10 phenol. Oxidation of the resultant product with potassium  
ferricyanide, followed by dehydrohalogenation with  
trimethylamine yielded the desired hexa-2,5-t-butyl  
triquino-cyclopropane.

15           The operational cell in the absence of an  
electric field, or any application of heat exhibited an  
absorbance maximum at about 620 nm, and appeared bright  
blue in color. This blue color was due to the absorbance  
of the isotropic dye alone, since the dichroic dye was in  
its low absorbance state. However, when a row heating  
20 pulse of 40 volts was applied for 6 milliseconds, the  
display in the heated area exhibited absorbance maxima at  
about 460 and 620 nm, and appeared a brilliant green. This  
green color was due to the additional absorbance of the  
dichroic dye which is now in its absorbing state. The  
25 application of an electric field while heating the display  
resulted in the original blue coloration.

## CLAIMS:

1. A composition of matter comprising a nematic, smectic or cholesteric liquid crystal material and at least one dichroic dyestuff, characterized in that said  
5 composition additionally comprises an isotropic dyestuff having the general formula

$$(Y)_n = C = (X)_m$$

wherein:

- 10 Y is independently selected from the group consisting of an anthracene-one group, a phthalate group, or a quinonoid benzene ring, provided that when Y is a quinonoid benzene ring, it is substituted with one or two alkyl substituents of about 1 to 20 carbon atoms in the ortho positions relative to the oxygen of  
15 the quinonoid benzene ring;

C is independently selected from the group consisting of a cyclopropyl and a cyclobutyl ring;

X is independently selected from the group consisting of A or an oxygen atom;

- 20 n is 1 to 3 when C is a cyclopropyl ring, and 1 to 4 when C is a cyclobutyl ring; and

m is 3-n when C is a cyclopropyl ring, and 4-n when C is a cyclobutyl ring,

- wherein said isotropic dyestuff has an optical order  
25 parameter of about 0.

2. The composition of Claim 1 further characterized by the feature that the concentration of said isotropic dyestuff is about 0.1 to 5 percent by weight of said liquid crystal material, and the concentration of said  
30 dichroic dyestuff is about 0.1 to 5 percent by weight of said liquid crystal material.

3. The composition of Claim 1 further characterized by the feature that there is additionally present an optically-active dopant in an amount sufficient  
35 to cholesterically order said composition of matter.

4. The composition of Claim 1 further characterized by the feature that said dichroic dye is a helichromic compound, said helichromic compound being a circularly dichroic dye having both a chromophoric moiety and an optically-active moiety, and said helichromic compound is present in said composition in an amount sufficient to enable said composition to propagate light in a circularly polarized manner.

5. A "guest-host" type liquid crystal display which is responsive to the absence or presence of an electric field, and which appears one color in the absence of said electric field and another color in the presence of said electric field, characterized by the feature that contained within said device is the composition of claim 1 wherein said liquid crystal material is a nematic liquid crystal material.

6. A "phase-change" type liquid crystal display device which is responsive to the absence or presence of an electric field, and which appears one color in the absence of said electric field and another color in the presence of said electric field, said device containing a composition comprising an optically active compound, characterized by the feature that said composition also comprises the composition of claim 1, wherein said liquid crystal material is a nematic liquid crystal material.

7. A "helichromic" type liquid crystal display device which is responsive to the absence or presence of an electric field, and which appears one color in the absence of an electric field and another color in the presence of said electric field, said device characterized by the feature that said composition comprises the composition of claim 4.

8. A thermally-addressable liquid crystal display device, which is responsive to the absence or presence of an electric field, and which appears one color in the absence of said electric field and another color in the presence of said electric field, said device comprising:

- a) a layer of a composition which has an absorption maximum between about 400 and 700 nm, said layer disposed between a top substrate and a bottom substrate, said composition being thermally sensitive and having a transition between at least two thermal phases, an upper phase being a nematic or isotropic phase and a lower thermal phase being a smectic phase, said composition having two possible states of orientation in said smectic phase, a first orientation state being a state in which said composition is substantially light absorbing and a second state being a state in which said composition is substantially light transmissive;
  - b) a means of affecting a thermal transition between said lower thermal phase and said upper thermal phase; and
  - c) a means of electrically addressing portions of said layer to develop said second orientation state when said composition passes rapidly into said lower thermal state from said upper thermal state, the remaining unaddressed portions of said layer developing said first orientation state when said composition passes rapidly into said lower thermal state from said upper thermal state;
- characterized by the feature that said composition is the composition of claim 1 wherein said liquid crystal material is a smectic liquid crystal material.

9. A thermally-addressable "cholesteric-smectic" type liquid crystal display device which is responsive to the absence or presence of an electric field, and which appears one color in the absence of said electric field and another color in the presence of said electric field, said device comprising:

a) a layer of a composition which has an absorption maximum between about 400 and 700 nm in admixture with an optically-active cholesteric compound, said layer disposed between a top substrate and a bottom substrate, said composition being thermally sensitive and having a transition between at least two thermal phases, an upper phase being a cholesteric or isotropic phase and a lower thermal phase being a smectic phase, said composition having two possible states of orientation in said smectic phase, a first orientation state being a state in which said composition is substantially light absorbing and a second state being a state in which said composition is substantially light transmissive;

b) a means of affecting a thermal transition between said lower thermal phase and said upper thermal phase; and

c) a means of electrically addressing portions of said layer to develop said second orientation state when said composition passes rapidly into said lower thermal state from said upper thermal state, the remaining unaddressed portions of said layer developing said first orientation state when said composition passes rapidly into said lower thermal state from said upper thermal state;

characterized by the feature that said composition is the composition of claim 1 wherein said liquid crystal material is a smectic liquid crystal material.

10. A thermally-addressable "helichromic-smectic" liquid crystal display device which is responsive to the absence or presence of an electric field, and which appears one color in the absence of said electric field and another color in the presence of said electric field, said device  
5 comprising:

- 10 a) a layer of a composition comprising an organic, nonionic, nonliquid-crystalline helichromic compound, said helichromic compound comprising at least one chromophoric moiety and at least one optically-active moiety, and said helichromic compound having an absorption maximum between about 400 and 700 nm, said layer disposed between a top substrate and a bottom substrate, said  
15 composition being thermally sensitive and having a transition between at least two thermal phases, an upper phase being a helichromic phase and a lower thermal phase being a smectic phase, said composition having two possible states of orientation in said smectic phase, a first  
20 orientation state being a state in which said helichromic compound is substantially light absorbing and a second state being a state in which said helichromic compound is substantially light transmissive;
- 25 b) a means of affecting a thermal transition between said lower thermal phase and said upper thermal phase; and
- 30 c) a means of electrically addressing portions of said layer to develop said second orientation state when said composition passes rapidly into said lower thermal state from said upper thermal state, the remaining unaddressed portions of said layer developing said first orientation state when  
35 said composition passes rapidly into said lower thermal state from said upper thermal state;



characterized by the feature that said composition is the composition of claim 1 wherein said liquid crystal material is a smectic liquid crystal material and wherein said dichroic dyestuff is said helichromic compound.